

Polymerization of Diglycidyl Ether of Bisphenol A/ Diaminodiphenyl Sulfone Epoxy Resins Using Radio Frequency Fields

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ABSTRACT: Curing of diglycidyl ether of bisphenol A/diaminodiphenyl sulfone (DGEBA/DDS) epoxy resin has been effected by heating with radio frequency (RF) radiation at frequencies of 30–99 MHz. The epoxy resins can be cured rapidly at low RF power levels. Comparison of the kinetics of the RF curing with thermal curing while maintaining the same curing temperature revealed no differences. Previous differences in rates of thermal and microwave curing are believed to be due to lack of temperature control during microwave curing. For RF curing, the rate of cure, at constant power level, increases at lower RF frequency, thus emphasizing one of the principal advantages of RF curing over microwave curing. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2917–2923, 1999

Key words: RF curing; epoxy resins; microwave curing

INTRODUCTION

A large number of commercially important polymerization processes are initiated by the application of heat to potentially reactive monomer species. Principal in importance of these systems are the epoxy resins. These materials are used in a wide range of areas, most notably as composite materials in marine and aerospace applications. For these uses large structures are often needed to be polymerized in one piece. The problems of maintaining a constant cure temperature, and hence a constant rate of cure and final cure, are not trivial. For example, in the aerospace industry, sophisticated and expensive bagging methods have been developed to ensure uniformity of cure.

Alternatives to these costly and difficult curing methods are therefore welcomed.

Over the past approximately 20 years there has been increased interest in the use of electromagnetic (EM) fields to inductively heat monomer resins to reaction temperature.^{1–23} The vast majority of the investigations reported in the open literature have been concerned with the use of EM radiation in the microwave region of the EM spectrum. The principal reason for this has been the availability of microwave sources in the form of commercial ovens. This work has demonstrated that curing of polymers such as epoxy resins,^{1,2,4,6–10,12–18,20,21} polyurethanes,^{5,11} vinyl polymers,^{3,19} and bismaleimides^{14,15} is indeed easily achievable using microwave fields. The possibility of very rapid curing of heterogeneous materials, and hence the formation of unique structures,^{14–16} has been canvassed by several workers. In addition, faster curing can often be achieved in resins,^{2,4,9,10} though the presence of glass fibres at high levels may slow the rate of cure. Pulsing of the microwaves appears to result

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in faster curing also.^{6-8,11,12} Despite the undoubted potential of this technology, there exists several points of contention between the various groups working in this area, which despite careful recent work does not appear to be fully resolved.

The first area of controversy arises from the comparison of the rates of curing achieved with microwave and conventional thermal methods. Several groups have claimed large increases in the rate of reaction using microwave compared with thermal curing.^{13,19-21} Critical evaluation of this work is, however, made more difficult by the absence of careful control of the temperature during microwave cure; meaningful comparison with thermal curing is therefore not possible. More recently, Mijovic and co-workers^{17,18} and Rogers²² have conducted careful studies of the kinetics of cure, in which the temperature achieved during the microwave cure was carefully matched with that in the thermal cure. Both groups have concluded that the kinetics of cure are essentially identical for the two methods of polymerization, and indeed Mijovic and Wiyaya¹⁷ have observed slightly lower rates of cure using microwaves.

A second area of controversy in this area is the mechanism of the curing reaction during microwave cure. Energy is transferred to the resin by coupling of the oscillating microwave electric field with the permanent dipoles in the resins. This has led to the concept of "hot spots" being formed around the functional groups containing large dipole moments,¹³ and therefore the possibility that specific groups may be "excited" in preference to other groups that do not contain large dipole moments. This attractive notion was suggested to account for the apparent large increase in rate of cure compared with thermal curing; however, as suggested above, recent work does not support an increased rate of curing using microwaves. Associated with this idea has been the suggestion that by varying the frequency of the microwave radiation, different groups may be excited. Examination of the dielectric loss spectra in the microwave region of typical resin mixtures, does not, however, reveal any structure or peaks in dielectric loss that may be associated with particular structures. It appears that the spectrum of absorption of energy extends over a very large range of frequencies in the microwave region, thereby precluding excitation of particular bands and hence structures.

This paper is concerned with the use of EM radiation of lower energy than microwaves, namely radiation in the radio frequency (RF) re-

gion of the EM spectrum. The reasons for using RF, as opposed to microwaves, are several. First, the dielectric loss of most resin materials is significantly larger in the RF region compared with the microwave. The dielectric spectrum tends to decrease fairly monotonically at frequencies greater than 1 MHz. Therefore, irradiation in the RF region (in our case 30-99 MHz) should result in much more efficient transfer of energy to the resin. It is well known that the power dissipation per unit volume during heating with EM radiation is proportional to both the frequency and the dielectric loss factor; the decrease in frequency on moving from microwave to RF frequencies is more than compensated for by the larger dielectric loss factor in the MHz range.²³ A second consideration is the wavelength of the respective radiations; RF has a longer wavelength (of the order of 3-10 m) compared with microwave (1-30 cm), and consequently the electric field should be more uniform in the RF case. Calculations indeed confirm this. One of the major problems of microwave curing, i.e., the nonuniformity of the electric field, is somewhat alleviated using RF, but not of course completely eliminated. A third associated advantage of RF over microwaves is the greater penetration of RF energy compared with microwave energy, thereby allowing the possibility of curing larger structures than with microwaves.

The aim of this paper is to demonstrate that the principles of curing of epoxy resins using EM radiation are also well obeyed in the RF region of the EM spectrum. The rates of cure using RF radiation are compared with the rates for thermal cure. The effect of RF frequency on the kinetics of cure is examined, as well as the power requirements for maintaining a constant cure temperature at different RF frequencies.

EXPERIMENTAL

Samples

Diaminodiphenyl sulfone (DDS) was obtained from Aldrich chemicals and recrystallized from a methanol/water mixture, then dried before use. Diglycidyl ether of bisphenol A (DGEBA) was Araldite GY260, having a formula weight of 374, and was used as supplied. Stoichiometric mixtures of the two materials were prepared and heated to 110°C with gentle stirring. At this temperature the samples were degassed by pumping under vacuum while continuing stirring for 10

mins. After degassing, the samples were transferred to thin-walled 5 or 10 mm Pyrex tubes.

Near Infrared

Near infrared (NIR) spectra were recorded using a Perkin-Elmer 1600 Fourier transform infrared (FTIR) spectrometer. FT-NIR spectra were recorded over a range of 7800 to 3500 cm^{-1} at a resolution of 8 cm^{-1} . For thermal cure an aluminum heating block, with an aperture to allow passage of the IR beam, was used.^{24,25} The temperature of the sample was monitored using an ASEA fiber optic temperature probe, which was inserted into a glass capillary tube, and then into the sample itself. For RF measurements, the enclosed RF coil was mounted on the FTIR optical bench, so that the FTIR beam passed through the sample adjacent to the ASEA temperature probe.

RF Heater

RF fields at 30–99 MHz were generated using a Schomandl ND 100 M frequency synthesizer. A 25 W Bruker broadband amplifier was used to generate and control the modest power levels used in this study (up to 5 W). The RF coils were home-built solenoid coils with from 5 to 10 turns and diameters of 5–10 mm, and with an adjustable Polyflon 5–20 pF capacitor for tuning the circuit for maximum absorption of RF energy. The coil was enclosed in a metal box with an aperture to allow the passage of the IR beam.

RESULTS AND DISCUSSION

Effect of RF Field on Temperature of Samples

In this paper epoxy resins have been inductively heated inside a simple solenoid RF coil operating at frequencies from 30–99 MHz. Great care was taken to ensure that the temperature inside the sample was close to that inside the thermally cured control samples. The initial set of experiments described immediately below, were conducted to examine the effect of RF power level on the temperature generated within the sample.

Figure 1 shows the temperature of the epoxy resin sample at the end of the ASEA temperature sensor, generated by continuous application of 54 MHz RF fields at power levels of 3.0, 3.5, and 4.0 W within solenoid coils of diameter of 10 mm. The rate of heating increased dramatically with increasing RF power. After less than 7 min, the

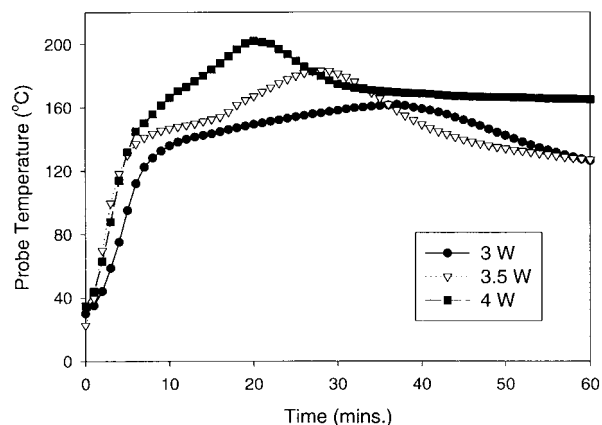


Figure 1 Temperature inside the epoxy resin sample during heating with RF fields at 54 MHz at power levels of 3.0 (●), 3.5 (▽), and 4.0 W (■) within 10 mm solenoid coils.

temperature had reached 130°C, where reaction began to occur. The temperature increased in a monotonic fashion until gelation occurred, and was followed by an increase in the rate of heating due to the reaction exotherm. At longer times the temperature decreased and attained an equilibrium value, which is a function of a range of parameters including the heat capacity of the total apparatus, the rate of heat flow from the sample, and the RF power level. Note that the time at which the gelation occurred decreased with increasing power levels. Similar behavior has been observed by Gourdenne and co-workers¹ during the microwave curing of DGEBA/DDM and polyester resins, and was analyzed in terms of a combination of the above parameters. Of particular interest is the very modest power levels (ca. 4 W) required to reach cure temperature using RF compared with power levels of >50 W used during the microwave curing. This difference reflects the greater absorption of energy at 54 MHz compared with 2.45 GHz, and is due to the much greater dielectric loss of the sample at the lower frequencies used here.

The appearance of a reaction exotherm in the temperature profiles in Figure 1 indicates that care should be taken to record the actual temperature during normal thermal cure. Figure 2 shows the temperature profile observed in the center of an epoxy resin sample placed into a heater block preheated to 170°C. A modest exotherm is observed at short times and the temperature in the sample reached 178°C after approximately 12 min. After gelation of the material the

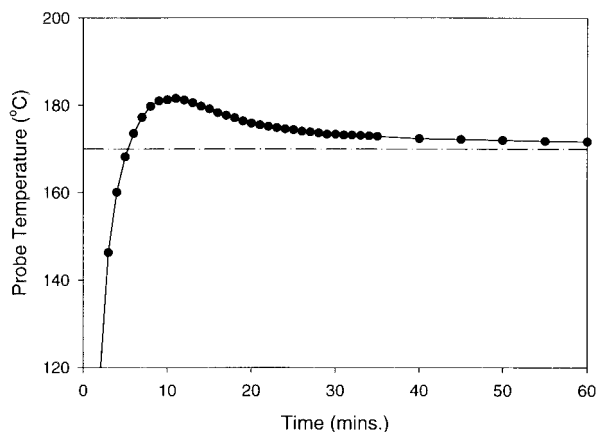


Figure 2 The temperature profile observed in the centre of an epoxy resin sample during curing in a heater block preheated to 170°C.

temperature dropped to an equilibrium value of 170°C. Care was taken to match this temperature profile when healing with RF radiation, by continual adjustment of the RF power level.

NIR Spectra of DGEBA/DDS

The NIR spectra of the epoxy resin before and after curing to full conversion are shown in Figure 3. The bands of importance are the primary amine combination band at 5067 cm^{-1} and the epoxy stretching band at 6060 cm^{-1} . Changes in the height and area of these bands, measured after baseline correction in a manner similar to that of George et al.,²⁴ were used to follow the changes in the concentration of the primary amine and epoxy group. The rate of formation of secondary amine groups was calculated from these results, and by assuming that etherification was not a major pathway for reaction of the epoxy groups.

Spectra recorded in the RF cell were of inferior quality to those reported by George et al. during thermal curing, due to the reduced path length resulting from the presence of the temperature sensor in the center of the sample tube. No attempt was therefore made to calculate the concentration of tertiary amine groups, or to follow the formation of hydroxyl groups.

Effect of Position of Temperature Sensor

The apparatus for *in situ* monitoring of the RF curing of the epoxy resin included the ASEA temperature probe inserted into the sample itself. It was found necessary for the center of the sensor

device to be placed precisely adjacent to the path of the FTIR beam. This is due to the presence of gradients in the electric field produced by this simple solenoid coil. Previously, other authors have acknowledged that inhomogeneous microwave fields may result in strong temperature gradients, and have consequent effects on the rate of polymerization of the resin (e.g., Ref. 16). The whole question of temperature control during polymerization by microwaves and RF is central to studies of the kinetics of reaction and comparisons with thermal cure. It was found, for example, that during these RF experiments moving the temperature probe 5 mm above the position of the NIR beam resulted in different reaction kinetics. The calculated electric fields for the simple solenoid coil used in these experiments is shown in Figure 4. The calculations were made using an iterative inverse finite Hilbert transform method.^{26,27} It should be emphasized that no attempt were made in this work to optimize the uniformity of the electric field; however, these modern methods provide much scope to achieve this aim if required. The temperature gradient on the reaction kinetics is made more pronounced by the large activation energy for reaction of primary amine in these systems.²⁴ Therefore, for all experiments discussed below, the center of the ASEA temperature sensor was positioned within the sample and within 0.1 mm of the NIR beam to minimize the effects of temperature gradients.

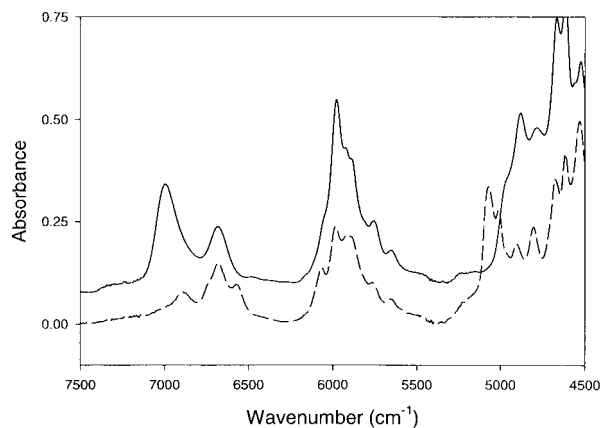


Figure 3 The NIR spectra of the DGEBA/DDS epoxy resin before (full line) and after curing at 170°C for one hour (broken line). The spectra have been offset by 0.1 absorbance units for clarity.

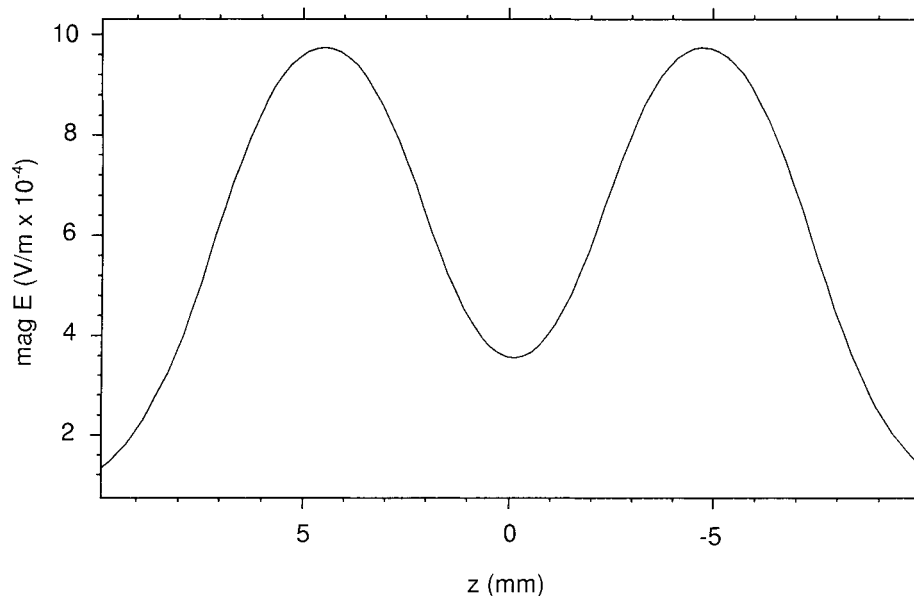


Figure 4 Calculated electric fields for the simple solenoid coil used in these experiments.²⁶

Kinetics of Reaction: Thermal Cure at 170°C vs RF Cure at 170°C

Figure 5 shows the relative concentration of primary amine, epoxy groups, and secondary amines during thermal cure at 170°C determined from measurement of the peak heights in the NIR spectra and calculation as described above. The corresponding results obtained during curing with the 30 MHz RF field is shown in Figure 6. It can be seen that the sets of results are essentially identical. This is in accord with the conclusions of

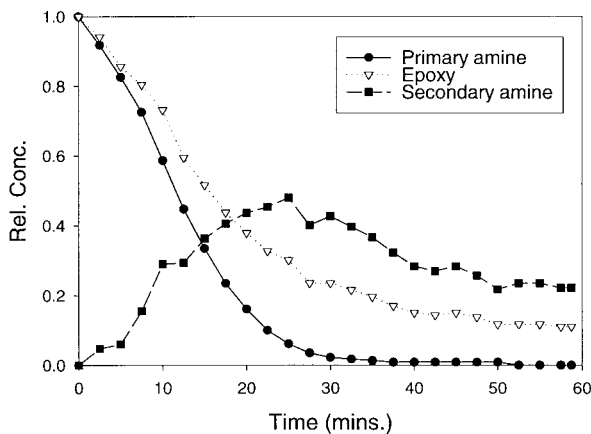


Figure 5 Relative concentration of primary amine (●), epoxy (▽), and secondary amines groups (■) during thermal cure at 170°C.

Mijovic et al.^{17,18} and Rogers²² that the cure kinetics are identical for thermal and EM curing, provided that care is taken to ensure that the temperatures achieved in both experiments are identical. In addition the rate of reaction of the secondary amine groups is also independent of heating method, indicating that the type of network formed should be similar in both cases.

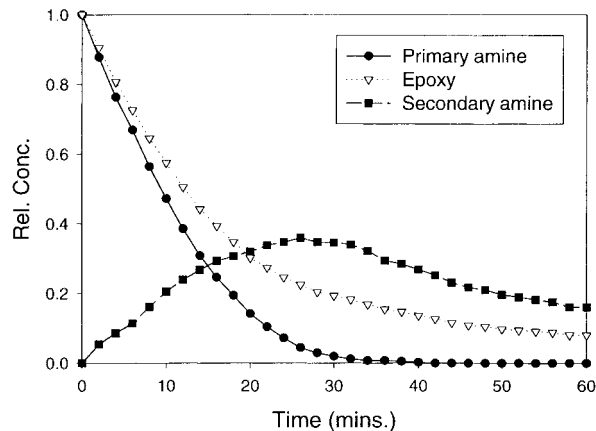


Figure 6 Relative concentration of primary amine (●), epoxy (▽), and secondary amines groups (■) during curing with RF radiation at 30 MHz with an average power level of 4.5 W, so as to maintain a temperature of 170°C.

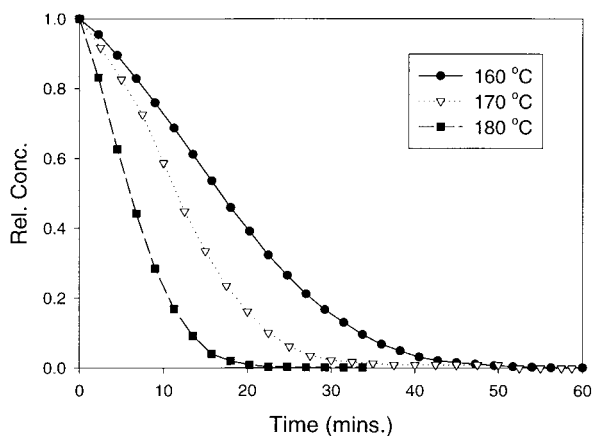


Figure 7 Relative concentration of primary amine groups measured during thermal cure at 160 (●), 170 (▽), and 180°C (■).

Kinetics of Thermal Cure at 160, 170, and 180°C

To underline the importance of precise temperature control, the rates of reaction have been measured during thermal cure at 160, 170, and 180°C. The corresponding plots of concentration of primary amine groups, during thermal cure at 160, 170, and 180°C are shown in Figure 7. This illustrates clearly that small differences in temperature can result in large differences in rate of reaction. It is suggested that the faster cure by microwave radiation compared with thermal cure reported previously is due to underestimation of the temperature generated within the sample.

Effect of Frequency of RF Radiation

Finally, the curing reaction was followed at three different RF frequencies to determine if the rates of reaction were dependent on frequency. The plots of concentration of reactive groups at the 54 and 99 MHz frequencies are identical to those at 30 MHz shown in Figure 5, and are not repeated here. Importantly, however, the power level required to achieve heating to 170°C increased at higher frequencies. An average power level of 0.85 W was required at 30 MHz, compared with 2.9 W at 50 MHz, and 4.75 W at 99 MHz (5 mm solenoid coils). This reflects the rapid decrease in dielectric loss of the resin at higher frequencies.

CONCLUSIONS

Radio frequency fields can be conveniently used to cure epoxy resin materials. When care is taken to

control precisely the temperature of reaction, the kinetics of reaction in the RF field are identical to those measured during conventional thermal cure at the same temperature. These results support the previous work of Mijovic and co-workers, and Rogers, performed with microwaves. As with microwave curing, thermal gradients produced in the sample by gradients in the RF electric fields can result in variations in rates of cure across the sample. The main advantages of the RF curing are the much lower power levels required to achieve rapid heating, superior penetration, and the possibility of design of RF coils with highly homogeneous RF fields.^{26,27}

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REFERENCES

- Gourdenne, A.; Maassarani, A. H.; Monchaux, P.; Aussudre, S.; Thourel, L. *Polym Prep* 1979, 20, 471.
- Gourdenne, A.; Van, Q. L. *Polym Prep* 1981, 22, 125.
- Teffal, M.; Gourdenne, A. *Eur Polym J* 1983, 19, 543.
- Gourdenne, A.; LePen, D.; Douibi, D. *Polym Prep* 1986, 27, 401.
- Silinski, B.; Kuzmycz, C.; Gourdenne, A. *Eur Polym J* 1987, 23, 273.
- Van, Q. L.; Gourdenne, A. *Eur Polym J* 1987, 23, 777.
- Beldjoudi, N.; Bouazizi, A.; Douibi, D.; Gourdenne, A. *Eur Polym J* 1988, 24, 49.
- Beldjoudi, N.; Gourdenne, A. *Eur Polym J* 1988, 24, 53.
- Baziard, Y.; Gourdenne, A. *Eur Polym J* 1988, 24, 873.
- Bouazizi, A.; Gourdenne, A. *Eur Polym J* 1988, 24, 889.
- Jullien, H.; Valot, H. *Polymer* 1985, 26, 506.
- Thullier, F. M.; Jullien, H.; Grenier-Loustalot, M. F. *Polym Commun* 1986, 27, 206.
- Lewis, D. A.; Hedrick, J. C.; Ward, T. C.; McGrath, J. E. *Polym Prep* 1987, 28, 330.
- Hedrick, J. C.; Lewis, D. A.; Ward, T. C.; McGrath, J. E. *Polym Prep* 1988, 29, 363.

15. Hedrick, J. C.; Lewis, D. A.; Lyle, G. D.; Ward, T. C.; McGrath, J. E. *Proc Am Soc Comp* 1988, 4, 167.
16. Marand, E.; Baker, K. R.; Graybeal, J. D. *Macromolecules* 1992, 25, 2243.
17. Mijovic, J.; Wijaya, J. *Macromolecules* 1990, 23, 3671.
18. Mijovic, J.; Fishbain, A.; Wijaya, J. *Macromolecules* 1992, 25, 986.
19. Palacios, J.; Sierra, J.; Rodriguez, M. P. *Polym Prep* 1991, 32, 244.
20. Wei, J.; Hawkley, M. C.; Delong, J. D.; Demeuse, M. *Polym Eng Sci* 1993, 33, 1132.
21. Wei, J.; Hawkley, M. C.; Demeuse, M. T. *Polym Eng Sci* 1995, 35, 461.
22. Rogers, D. G. Ph.D. thesis, University of Queensland, 1996.
23. Jones, P. L.; Rowley, A. T. *Drying Technol* 1996, 14, 1063.
24. George, G. A.; Cole-Clarke, P.; St. John, N.; Friend, G. *J Appl Polym Sci* 1991, 42, 643.
25. Hill, D. J. T.; George, G. A.; Pomery, P. J.; Rogers, D. G.; Carswell, T. G. *Polym Mater Sci Eng* 1992, 66, 297.
26. Crozier, S.; Forbes, L. K.; Roffmann, W. U.; Leuscher, K.; Doddrell, D. M. *Concepts Magn Reson* 1997, 9, 195.
27. Mahony, C.; Forbes, L.; Crozier, S.; Doddrell, D. M. *J Magn Reson* 1995, 107, 145.